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Doming Modes and Dynamics of Model Heme Compounds

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Beamline: U2A

Introduction:. An outstanding important problem in the understanding of physiological functions is that of protein dynamics. In particular, the transportation of oxygen via the heme protein is controlled by the dynamics of this type of molecule. There have been numerous studies using various techniques [1-3] with the goal of characterizing the dynamics of heme compounds that are models for myoglobin but a definitive characterization ofthe dynamics and of specific vibrational modes has been challenging.

In our experiments, we have used a unique combination of far-infrared and high pressure techniques together with state-of-the-art quantum chemistry methods to characterize the dynamics of model heme proteins. The most important vibrational mode and the one that has received the most intensive study is that of the "doming" mode in which an iron atom moves out of the plane of the poriphyrin molecular plane while the periphery of this ring moves in the opposite direction. This mode is infrared active but could not be observed experimentally due to its low frequency and weak absorptivity. In our experiments, we have used a unique combination of synchrotron far-infrared and high pressure techniques together with state-of-the-art quantum chemistry methods to characterize the dynamics of model heme proteins.

Methods and Materials: The sample COFe(OEP)Py (carboxy-octaethyl-ironporphyrin Pyridine) was prepared as described in reference 4. It was mounted in a diamond anvil cell equipped with very thick steel gaskets (up to 500 microns thick) with large diameter holes (up to 800 microns in diameter). Spectra were obtained as a function of pressure on beamline U2A. The pressure was measured by the wavelength shifts of the ruby fluorescence from ruby chips loaded with the sample.

Calculations were performed using gradient-corrected DFT methods [4]

Results: The far-infrared spectra obtained as a function of pressure provided a method, when combined with high level quantum calculations, of identifying the “doming” mode as well as other vibrational modes for the model heme compound. The doming mode with its expected high pressure dependence was identified at 53 cm^-1. Related normal modes were also identified.

Conclusions: The use of synchrotron infrared spectroscopy and high pressure techniques, together with high-level quantum chemistry calculations has enabled the identification of low-frequency modes including the “doming” mode for a model heme compound.

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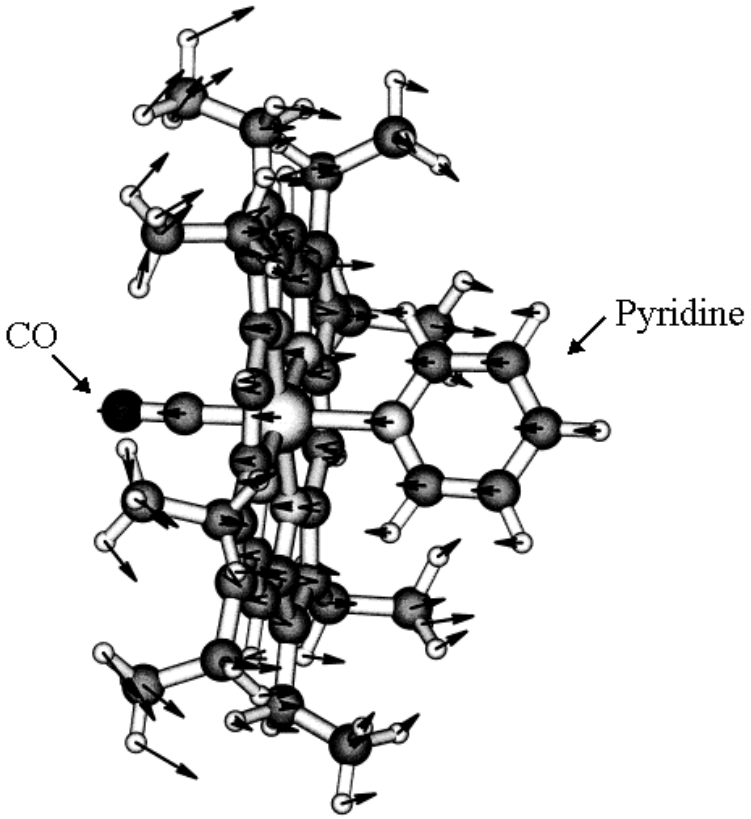

The model heme molecule showing atom displacements for the doming mode